

CRYSTALLIZATION IN CERAMICS

BY

ARTHUR LEROY FRIEDBERG

B.S., University of Illinois, 1941

M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CERAMIC ENGINEERING IN THE GRADUATE COLLEGE
OF THE UNIVERSITY OF ILLINOIS, 1952

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CRYSTALLIZATION IN CERAMICS

The crystallization processes in ceramic systems often involve the nucleation and growth of crystals from very viscous liquids. This crystal formation in viscous ceramic melts presents a unique condition that is characterized by the sluggishness of crystallization and the associated tendency for glass formation.

The factors significant to the crystallization behavior in ceramic systems include mainly the composition and viscosity of the melts, the amount of supercooling or supersaturation, and the subsequent heat treatments given the cooled material.

A study pertaining to the crystallization behavior in titanium opacified porcelain enamels was undertaken with specific interest on the effect of firing temperature and time on the crystallization of the opacifying phase in the enamels. Titanium enamels of the type in which opacity is principally developed during the firing of the enamel have shown an instability or sensitivity in the color of the fired enamel. The color is sensitive not only to compositional changes of the enamel but also to the smelting and firing treatments.

The fired enamel represents essentially a glass-particle system in which the crystalline particles are suspended and dispersed in the glass matrix. The small size of these particles and the great difference in optical properties of the particles and glass are responsible for the diffusion and scattering of the light incident on this system. In this investigation, the nature of the opacifying crystals as a function of firing temperature and time was studied in relation to the spectrophotometric characteristics of the fired titanium enamels.

EXPERIMENTAL PROCEDURE

Since the color of the fired titanium enamel changed with different firing treatment, the size of the opacifying crystal was considered one of the main factors influencing this color change. Three different titanium enamel compositions were made and fired at varying times and temperatures.

Spectrophotometer curves were made of all enamel panels. Specimens cut from each panel were used for the x-ray analysis of the relative amounts of titania crystals (anatase and rutile) in the fired enamel. The panels were then prepared for electron microscope studies. Opacifying particles in the titanium enamels were freed from

the enamel surface by etching for ten seconds with hydrofluoric acid. A powder of crystals was then removed from the enamel surface and viewed in the electron microscope.

DISCUSSION OF RESULTS

(1) Electron micrographs of the crystals in the titanium enamels indicated the shape of rutile particles as needle- or stick-shaped particles and anatase particles as irregularly-shaped rounded particles. Changes in firing temperature affected the size of opacifying particles more than changes in firing time. Comparing anatase and rutile, the rutile particles showed the greater increase in size with increasing firing temperature.

(2) As firing temperature or firing time was increased (a) the amount of anatase crystals decreased and the amount of rutile crystals increased, and (b) a change from a blue-white to a cream-white color was observed.

(3) The blue-white color of enamels fired at the lower temperatures was caused by the scattering of blue light (Rayleigh Scattering) by the very small opacifying particles in the fired enamel. As firing temperature was increased, the size of the opacifying particles increased, the scattering of blue light decreased, and the fired enamel became less blue and more cream-white in color.

(4) In the enamels containing both anatase and rutile, the smallest anatase particles were predominant at the lower firing temperatures. As firing temperature was increased, the amount of anatase decreased and the larger rutile crystals predominated. The sharpest changes in the color of the fired enamel occurred between 1500 and 1600° F., in which range the relative amounts of anatase and rutile changed greatly.

VITA

Arthur Leroy Friedberg was born March 25, 1919 in River Forest, Illinois. He attended the public schools in Yorkville, Illinois, graduating from the Yorkville High School in June, 1937. He entered the University of Illinois in September of that year, and received the degree of Bachelor of Science in Ceramic Engineering in June, 1941. Until February, 1943, when he enlisted for military service, he was employed by the Stone and Webster Engineering Corporation and by the War Department. As an Aerological Officer in the United States Navy, he served in the Pacific Area. In the course of naval training, he attended the University of Chicago and Scripps Institute of Oceanography. After being released to inactive duty in February, 1946, he returned to the Graduate College of the University of Illinois, and received his Master's Degree in Ceramic Engineering in February, 1947. He continued his graduate work until June of that year, after which time and until September, 1950, he was employed as Research Associate in the Department of Ceramic Engineering. In the academic year, 1950-51, he again entered the Graduate College and held a Departmental Fellowship.

Publications are:

"Effect of Composition on Properties of Titanium Enamels," (with F. A. Petersen and A. I. Andrews), *J. Am. Ceram. Soc.*, **30**, 261-277 (1947).

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